

# PATENT SPECIFICATION

(11) 1 282 506

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## DRAWINGS ATTACHED

- (21) Application No. 38478/69 (22) Filed 31 July 1969  
 (23) Complete Specification filed 22 July 1970  
 (45) Complete Specification published 19 July 1972  
 (51) International Classification C22B 53/00  
 (52) Index at acceptance

C1N 212 213 232 233 246 248 251 261 264 269 275  
 337 347 34X 351 353 35X 35Y 367 395 396  
 397 402 403 406 407 408 414 415 41X 420 422  
 42X 42Y 432 433 435 436 440 448 449 464  
 477 491 492 501 504 508 510 511 515 516 52Y  
 543 553 555 556 580 581 588 58X 591 592 593  
 594 597 604 613 617 619 61X 61Y 620 622 623  
 625 62Y 630 632 633 636 63X 663 675 69X  
 729 730 775 780 78X

C1A D10 G13 G13D10 G34 G34D10 N13A

- (72) Inventors FRANK RONALD WILLIAMS, JACK WHITEHEAD,  
 JEFFERSON MARSHALL, ALAN CONNERS and  
 DEREK VERNON GOSDEN

## (54) A PROCESS FOR THE REMOVAL OF IRON IN THE BENEFICIATION OF AN IRON-CONTAINING TITANIFEROUS MATERIAL

(71) We, BRITISH TITAN LIMITED,  
 formerly British Titan Products Company  
 Limited, a British Company, Billingham,  
 Teesside, Great Britain, do hereby declare  
 5 the invention for which we pray that a patent

is to be used in the production of titanium  
 tetrahalides such as titanium tetrachloride by  
 halogenation, for example in a fluidised bed.

It is an object of the present invention to 40  
 achieve these aims

## PATENTS ACT 1949

## SPECIFICATION NO 1282506

A statutory reference was made by the Superintending Examiner acting for the Comptroller General on  
 18 November 1976 under Section 14 in the following manner:—

Reference has been directed, in pursuance of Section 9 subsection (1) of the Patents Act 1949 to  
 Specification No 1225826

## THE PATENT OFFICE

2 March 1977

Bas 32870/9

25 tion of ferrous chloride which is particularly  
 suitable for conversion to finely-divided iron  
 via reduction of solid ferrous chloride di-  
 hydrate or to finely-divided iron oxide). The  
 hydrochloric acid may be recovered from such  
 material, for example, by the Aman process  
 30 (as described in British specification 793,700).

During the leaching step, it is important on  
 a commercial scale to remove as much as  
 possible of the iron content from, and to re-  
 cover as much as possible of the titanium  
 35 dioxide content in, the final solid product. This  
 is particularly true if the beneficiated product

It is preferred that the starting material 60  
 should have an average mean weight particle  
 size in the range of 50 $\mu$  to 300 $\mu$  and particu-  
 larly one in the range 100 $\mu$  to 200 $\mu$ .

The material may be heated, for example,  
 to a temperature in the range 850°C to 950°C in an oxidising atmosphere such as air 65  
 for a sufficient length of time to convert sub-  
 stantially all the iron content to the ferric  
 state. This may be accomplished, in a rotat-  
 ing kiln or in a fluidised bed or in other suit- 70  
 able device.

After oxidation the iron content of the

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(72) Inventors FRANK RONALD WILLIAMS, JACK WHITEHEAD,  
JEFFERSON MARSHALL, ALAN CONNERS and  
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## (54) A PROCESS FOR THE REMOVAL OF IRON IN THE BENEFICIATION OF AN IRON-CONTAINING TITANIFEROUS MATERIAL

(71) We, BRITISH TITAN LIMITED, formerly British Titan Products Company Limited, a British Company, Billingham, Teesside, Great Britain, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the beneficiation of iron-containing titaniferous materials such as ilmenites or leucoxenes.

It has been found desirable, when beneficiating iron-containing titaniferous materials to preheat the material under oxidising conditions to ensure that the iron content is in the ferric state and thereafter to reduce the iron substantially wholly to the ferrous state. By this means the iron content of the material is rendered more reactive when contacted with a mineral acid such as aqueous hydrochloric acid (when the iron content is removed as a solution of ferrous chloride which is particularly suitable for conversion to finely-divided iron via reduction of solid ferrous chloride dihydrate or to finely-divided iron oxide). The hydrochloric acid may be recovered from such material, for example, by the Aman process (as described in British specification 793,700).

During the leaching step, it is important on a commercial scale to remove as much as possible of the iron content from, and to recover as much as possible of the titanium dioxide content in, the final solid product. This is particularly true if the beneficiated product

is to be used in the production of titanium tetrahalides such as titanium tetrachloride by halogenation, for example in a fluidised bed.

It is an object of the present invention to achieve these aims.

Accordingly, the present invention is a process which comprises heating a finely-divided, iron-containing titaniferous material under oxidising conditions to convert the iron content to the ferric state, reducing the iron content substantially wholly to the ferrous state and thereafter firstly contacting the material with aqueous hydrochloric acid containing dissolved titanium from a previous leaching step and with fresh aqueous acid to leach out the iron content of the material before recovering finely-divided solid material containing an increased proportion of titanium dioxide.

The starting material for the present process may be, for example an ilmenite or a leucoxene and is preferably the former. Such materials usually contain between 5% and 55% of iron (as FeO).

It is preferred that the starting material should have an average mean weight particle size in the range of  $50\mu$  to  $300\mu$  and particularly one in the range  $100\mu$  to  $200\mu$ .

The material may be heated, for example, to a temperature in the range  $850^{\circ}\text{C}$  to  $950^{\circ}\text{C}$  in an oxidising atmosphere such as air for a sufficient length of time to convert substantially all the iron content to the ferric state. This may be accomplished, in a rotating kiln or in a fluidised bed or in other suitable device.

After oxidation the iron content of the

material is reduced until it is substantially wholly in the ferrous state, i.e. not more than 2% by weight of the iron content (estimated as Fe) should be present as ferric iron or as metallic iron.

The reducing agent may be solid carbon but is preferably a gaseous reducing agent such as hydrogen (with or without the introduction of a minor proportion of steam) a hydrocarbon containing from 1 to 4 carbon atoms, particularly methane as described, for example, in our copending applications 38475/69 and 38474/69 (Serial Nos. 1,282,503 and 1,282,324). The reduction is conveniently carried out at a temperature in the range 600°C to 1,100°C and particularly at one in the range 700°C to 900°C.

Any suitable apparatus may be used for the reduction but it is again preferred to utilise a fluidised bed or a rotating kiln.

After reduction the material is subjected to a two stage leaching in which the reduced material is separately contacted with suitable quantities of aqueous hydrochloric acid, the first of which contains dissolved titanium.

The first leach is carried out using aqueous hydrochloric acid which has been used to leach a preceding batch of reduced iron-containing titaniferous material. Such once-used acid contains dissolved titanium (and iron) and has the advantage that it dissolves less titanium when used as a first leaching liquid of a new batch of reduced iron-containing titaniferous material. Normally, the acid contains an amount of titanium in the range of 0.01% to 2.0% and particularly from 0.2% to 2.0% by weight (estimated as  $\text{TiO}_2$ ) and an amount of iron in the range of 10% to 20% by weight (estimated as FeO).

A stoichiometric excess of acid (based on the iron content of the reduced material before leaching) is preferably used, for example 20% to 30% excess, and the leaching is carried out at an elevated temperature, for example at a temperature in the range 80°C to that of the boiling point of the acid since such temperatures also assist significantly in reducing the amount of titanium which is rendered soluble during leaching. The leaching may also be carried out under superatmospheric pressure, if desired.

The solid material is then separated from the suspension, for example after a period of 30 to 300 minutes, and is then conveniently contacted with a similar amount of acid, e.g. 20% to 30% stoichiometric excess based on the iron content of the reduced material before leaching at similar temperatures until substantially all the iron content has been removed. This leach is carried out with fresh aqueous hydrochloric acid (which is then re-used in the first leaching stage of a subsequent batch of reduced iron-containing titaniferous material).

The aqueous hydrochloric acid used may

be of any strength which will leach out the iron content of the material in a commercially acceptable time but it is preferred to use acid containing from 18% to 22% by weight of HCl, at least when leaching with fresh acid. The  $\text{TiO}_2$  content of the intermediate solid product of the two stage leaching process is normally in the range 75% to 85%.

After treatment by the process of the present invention the solid product (which may be recovered by filtration, by the use of a centrifuge or by decantation) generally has a titanium content (estimated as  $\text{TiO}_2$ ) of at least 90% and normally of at least 95% and preferably of at least 96% and is very suitable, particularly after a calcination step for chlorination in a fluidised bed to titanium tetrachloride.

It has been found that mechanical agitation during the leaching stages is most undesirable since it leads to breakdown of the leached particles, thereby rendering at least some of them difficult to recover and of unsuitable size for halogenation, at least in a fluidised bed.

Consequently agitation (which is normally necessary for adequate leaching) may conveniently be provided by passing a gas, for example nitrogen or other inert gas, through the suspension of solids in liquid.

It has also been found particularly convenient to contact the reduced iron-containing titaniferous material with acid in a fluidised column in which the acid is passed upwardly through the column thereby contacting and fluidising the material in the column. The acid used in such a process is normally recycled through the column a number of times before being used for leaching a subsequent batch of reduced material, or discarded, as desired.

In the following Examples, Example 1 describes a process of the present invention using a fluidised column for leaching. Example 2 describes a process not according to the present invention into which the material is subjected, under conditions similar to those in Example 1, to a single leaching stage only.

#### EXAMPLE 1

Three hundred gram portions of an ilmenite containing 56.5% titanium (expressed as  $\text{TiO}_2$ ) and 40.7% iron (expressed as FeO) which had been oxidised and reduced to ferrous iron at 875°C were taken and treated as indicated at A, F, K, P and U in the flow sheet shown in the Figure accompanying the Provisional specification.

The material was contacted with the acid in the leaching steps in a column up which was passed aqueous hydrochloric acid at a rate of 10 ml/second. This was collected from the top of the column and recirculated through the column for 60 minutes.

The fresh acid (designated as leach N.A.) was constant boiling acid (at atmospheric

pressure) and both fresh and once-used acid were circulated at a temperature of 100°C.

Sufficient *fresh* acid was used at each stage to provide a 20% stoichiometric excess (based on the iron content of the starting material).

The titanium content as *soluble* and *insoluble* TiO<sub>2</sub> was estimated for the *Discard Liquor* (C) and the *Final Liquors* H, M, R

and W (also with the HCl content) and the titanium and iron content (expressed as TiO<sub>2</sub> and FeO respectively) of the *Product Solids* D, I, N and S and *Intermediate Solids* B, G, L, Q, & V were also estimated. The TiO<sub>2</sub> content of Q is given as a typical value for the Intermediate Solids. The results are given in the Table below:

TABLE

Discard Liquor (C)			
Soluble TiO <sub>2</sub> g/l		5.6	
Insoluble TiO <sub>2</sub> g/l		5.5	
Total Fe g/l		76.5	
Product Solids	Weight g.	TiO <sub>2</sub> %	Fe %
Stage D	153	96.3	0.35
Stage I	168	96.1	0.39
Stage N	170	96.8	0.62
Stage S	166.5	96.0	0.78
Intermediate Solids (Q)			
TiO <sub>2</sub> %		81.2	
Weight g		208.2	
Final Liquor	Sol. TiO <sub>2</sub>	Insol. TiO <sub>2</sub>	HCl
Stage H	0.69	3.27	5.0
Stage M	0.63	3.81	5.4
Stage R	2.19	6.90	5.5
Stage W	0.39	3.00	6.2

## EXAMPLE 2

Three hundred grams of an ilmenite containing 56.5% titanium (expressed as TiO<sub>2</sub>) and 40.5% iron (expressed as FeO) which had been oxidised and reduced at 875°C were leached for 2 hours at 100°C in a vessel with 20% stoichiometric excess of constant boiling aqueous hydrochloric acid. Agitation was provided by bubbling nitrogen through the mixture.

The leached material was then recovered and analysed for titanium and iron.

The product contained only 89.3% titanium (expressed as TiO<sub>2</sub>) and 4.8% iron (expressed as FeO). These figures should be compared with those for the *Product Solids* shown in the Table of Example 1 (96% to 96.8% TiO<sub>2</sub> and 0.35% to 0.78% FeO).

## WHAT WE CLAIM IS:—

1. A process comprising heating a finely-divided iron-containing titaniferous material under oxidising conditions to convert the iron

content to the ferric state, reducing the iron content substantially wholly to the ferrous state and thereafter firstly contacting the material with aqueous hydrochloric acid containing dissolved titanium from a previous leaching step and then with fresh aqueous acid to leach out the iron content before recovering finely-divided solid material containing an increased proportion of titanium dioxide.

2. A process as claimed in claim 1 wherein the finely-divided iron-containing material has an average mean weight particle size in the range of 50μ to 300μ and preferably one in the range 100μ to 200μ.

3. A process as claimed in claim 1 or 2 in which the finely-divided iron-containing titaniferous material is heated under oxidising conditions to a temperature in the range 850°C to 950°C to oxidise the iron content to the ferric state.

4. A process as claimed in any of the preceding claims in which the oxidised finely-

- divided iron-containing titaniferous material is heated under reducing conditions to a temperature in the range 600°C to 1,100°C and preferably to a temperature in the range 700°C to 900°C.
- 5 5. A process as claimed in any of the preceding claims wherein the titanium-containing aqueous hydrochloric acid contains an amount of titanium in the range 0.01% to 2% and preferably an amount in the range 0.2% to 2% by weight, estimated as  $TiO_2$ .
- 10 6. A process as claimed in any of the preceding claims wherein sufficient aqueous hydrochloric acid is used in each stage to provide a 20% to 30% stoichiometric excess based on the iron content of the reduced material before leaching.
- 15 7. A process as claimed in any of the preceding claims wherein the leaching is carried out at a temperature in the range 80°C to the boiling point of the acid.
- 20 8. A process as claimed in any of the preceding claims in which the oxidised and reduced material is leached in the first stage with aqueous hydrochloric acid for a period of from 30 to 300 minutes.
- 25 9. A process as claimed in any of the preceding claims wherein the fresh aqueous hydrochloric acid contains from 18% to 22% by weight of HCl.
- 30 10. A process as claimed in any of the preceding claims wherein the iron-containing titaniferous material after the first stage leach contains from 75% to 85% by weight of titanium, expressed as  $TiO_2$ .
- 35 11. A process as claimed in any of the preceding claims wherein the titaniferous material is agitated, during leaching, by passing a gas through the suspension of solids in the liquid.
- 40 12. A process as claimed in any of the preceding claims wherein the acid is passed upwards through a column of the material to be leached.
- 45 13. A process as claimed in claim 12 wherein the acid is recycled through the column.
14. A process as claimed in any of the preceding claims and substantially as described in Example 1.
- 50 15. Finely-divided solid titanium dioxide-containing material when prepared by a process claimed in any of the preceding claims.

JOHN RUSSELL,  
Agent for the Applicants.

